THE METAL CARBONYLS

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A MAJOR obstacle to the successful production of chlorine by the Solvay process was the very rapid corrosion of the nickel valves in the brick-lined tanks in which ammonium chloride was vapourized. A laboratory study of the corrosion showed it to be due to the presence of small amounts of carbon monoxide in the carbon dioxide stream used to sweep out ammonia from the tanks.[1] A more elaborate study of the interaction of carbon monoxide and metallic nickel led to the now classical discovery[2] in 1890 of nickel tetracarbonyl. Such was the extremely unusual nature of the compound that it immediately attracted the attention of many distinguished chemists of the day.

It is one of the interesting coincidences of science that, on June 15th, 1891, Mond[3, 4] in London and Berthelot[5] in Paris were addressing respectively the Chemical Society and the Academy of Sciences upon their independent discoveries of iron carbonyl, the next member of this new class of compounds. Since this date the number of known metal carbonyls has increased steadily.

As previous review articles[6-13] cover adequately the state of knowledge of the metal carbonyls at intervals in the past, it is proposed, in general, to summarize here only some of the more recent advances in knowledge of the binary metal carbonyls.

The tremendous increase in interest in the metal carbonyls over the last decade has arisen partly as a result of the discovery of many novel organometallic compounds, in which a metal carbonyl system forms an integral part of the structure. A number of recent books and review articles well illustrate their remarkable variety.[6-18]

[1] Mond, *J. Soc. Chem. Ind.*, 1895, **14**, 945.
[2] Mond, Langer, and Quinke, *J.*, 1890, **57**, 749.
[3] Mond and Quinke, *Chem. News*, 1891, **63**, 301.
[4] Mond and Langer, *J.*, 1891, 1090.
[5] Berthelot, *Compt. rend.*, 1891, **112**, 1343.
[6] Hieber, *Z. Elektrochem.*, 1937, **43**, 390; *Die Chemie*, 1942, **55**, 7.
[7] Blanchard, *Chem. Rev.*, 1937, **21**, 3.
[8] Wardlaw, *Ann. Reports*, 1934, **31**, 99.
[9] Trout, *J. Chem. Educ.*, 1937, **14**, 453, 575; 1938, **15**, 77, 113.
[10] Welch, *Ann. Reports*, 1941, **38**, 71.
[11] Anderson, *Quart. Rev.*, 1947, **1**, 33.
[12] Cable and Sheline, *Chem. Rev.*, 1956, **56**, 1.
[13] Chatt, Pauson, and Venanzi, in "Organometallic Chemistry", ed. Zeiss, Reinhold, New York, 1961, p. 468.
[14] Pauson, *Proc. Chem. Soc.*, 1960, 297; *Endeavour*, 1962, **21**, 175.
[15] Wilkinson and Cotton, in "Progress in Inorganic Chemistry", ed. Cotton, Interscience Publ., Inc., New York, 1959, Vol. I, p. 1.
[16] Fischer and Fritz, in "Advances in Inorganic and Radiochemistry", ed. Emeléus and Sharpe, Academic Press, New York, 1959, Vol. I, p. 55.
[17] Coates, "Organometallic Compounds", Methuen and Co., London, 2nd edn., 1960.
[18] Guy and Shaw, in "Advances in Inorganic and Radiochemistry", ed. Emeléus and Sharpe, Academic Press, New York, 1962, Vol. IV, p. 77.

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Preparation of Carbonyls.—Only nickel, iron, and cobalt appear to react directly with carbon monoxide to give the carbonyls.[13] In other cases suitable salts or complexes of the metal are reduced in the presence of carbon monoxide. The choice of conditions for temperature and pressure is often critical, as also is the selection of metal derivative and reductant. The earlier reactions used in these preparations are already well documented,[11] and are still widely used. In recent years, however, many novel methods have been invoked to obtain good yields of some of the previously more inaccessible metal carbonyls.

The carbonylation of chromous or chromic acetylacetonate or certain organic salts (*e.g.*, acetate), in the presence of powdered zinc or magnesium, with pyridine as solvent, gave 80—90% yields of chromium hexacarbonyl.[19] Essentially the same method, with vanadium trichloride or oxide trichloride or vanadium(III) acetylacetonate in place of chromium compounds gave 40—50% yields of vanadium hexacarbonyl.[20] The carbonylation of chromic chloride takes place in the presence of aluminium chloride, powdered aluminium, and benzene, to produce an 88% yield of the hexacarbonyl;[21] it is likely that dibenzenechromium is an intermediate in this reaction, in the same way as phenylchromium compounds are believed[22] to be intermediates in Job and Cassal's Grignard synthesis of chromium hexacarbonyl.[23]

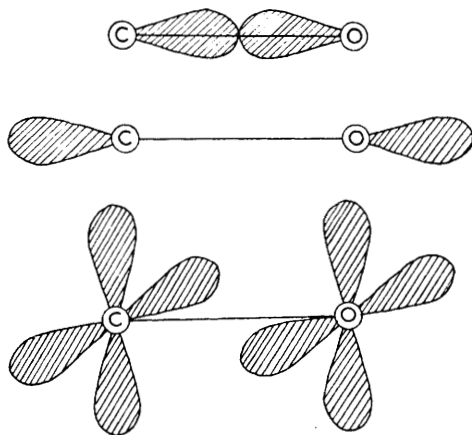Triethylaluminium has been used in ether to reduce various metal

FIG. 1. *Bonding orbitals in carbon monoxide.*

[19] Natta, Ercoli, Calderazzo, and Rabizzoni, *J. Amer. Chem. Soc.*, 1957, **79**, 3611.
[20] Ercoli, Calderazzo, and Alberola, *J. Amer. Chem. Soc.*, 1960, **82**, 2966.
[21] Fischer, Hafner, and Öfele, *Chem. Ber.*, 1959, **92**, 3050.
[22] Zeiss, in "Organometallic Chemistry", ed. Zeiss, Reinhold, New York, 1960, p. 417.
[23] Job and Cassal, *Compt. rend.*, 1926, **183**, 58.

salts for subsequent carbonylation in good yield.[24] The same reaction, with hydridodibutylaluminium in place of triethylaluminium has also been noted.[25] Lithium aluminium hydride, as a reductant of chromic chloride, is reported to lead to a 65% yield of the hexacarbonyl on carbonylation.[26] Metallic sodium in diethyleneglycol dimethyl ether has been found to give high yields of all the Group VI metal hexacarbonyls by reductive carbonylation of chromium(III), molybdenum(V), and tungsten(VI) chloride, respectively.[27]

Manganese carbonyl, originally reported[28] in only 1% yield, can now be obtained in a 32% yield by using sodium benzophenone ketyl as reductant before carbonylation,[29] and the same method also produced a 60% yield of chromium carbonyl.

Although not strictly a carbonylation from carbon monoxide itself, the metathetical reactions of iron pentacarbonyl with molybdenum pentachloride and with tungsten hexachloride gave, respectively, molybdenum hexacarbonyl (28% yield) and tungsten hexacarbonyl (85% yield).[30]

Bonding in the Metal Carbonyls.—(a) *The carbon–oxygen bond.* In carbon monoxide there are three occupied σ-orbitals.[31] These correspond to the σ-bond [(a) in Fig. 1] between the two atoms, and the lone pairs of electrons [(b) in Fig. 1], on the carbon and oxygen atoms. In addition, there is a doubly degenerate bonding π-orbital [(c) in Fig. 1]. The result is a triple bond $(\sigma)^2(\pi_y)^2(\pi_x)^2$. It should be emphasised, however, that this qualitative picture is a considerable over-simplification of the final atomic populations. In particular, the oxygen lone-pair orbital is not believed to be as strongly directed as the corresponding lone-pair orbital of carbon, which is almost entirely a digonal $C(2s)$–$C(2p_x)$ hybrid. Further, in the π-orbitals the electrons are about four times as likely to be near oxygen as near carbon, making this a fairly polar bond. It is as a result of this asymmetry in the π-orbitals that the bond strength is considerably lower than in a similar homopolar triple bond such as that in N_2. The low dipole moment of carbon monoxide is believed to be mainly explained by this bond-polarity's compensating the strongly directional lone pair on the carbon atom.

(b) *The metal–carbon bond.* Carbon monoxide does not appear to be basic, and the donor power of the lone pair of electrons on the carbon

[24] Podall, *J. Amer. Chem. Soc.*, 1958, **80**, 5573.
[25] Zakharkin, Gavrilenko, and Okhlobystin, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1958, 100.
[26] Nesmeyanov, Anisimov, Volkov, Fridenburg, Mikheev, and Medvedeva, *Zhur. neorg. Khim.*, 1959, **4**, 1827.
[27] Podall, Prestridge, and Shapiro, *J. Amer. Chem. Soc.*, 1961, **83**, 2057.
[28] Brimm, Lynch, and Sesney, *J. Amer. Chem. Soc.*, 1954, **76**, 3831.
[29] Closson, Buzbee, and Ecke, *J. Amer. Chem. Soc.*, 1958, **80**, 6167.
[30] Nesmeyanov, Anisimov, Mikheev, Volkov, and Valueva, *Zhur., neorg. Khim.*, 1959, **4**, 249, 503.
[31] Coulson, "Valence", Oxford University Press, 2nd edn., 1961, p.222.

atom can only be slight, as illustrated by the absence of simple complexes with the normal vacant-orbital acceptors. A sole exception to this is the rather unstable [32] complex, H_3B,CO.

In the metal carbonyls,[33] the overlap of the lone pair on the carbon atom with the nd, $(n + 1)s$, and $(n + 1)p$ vacant metal orbitals may be regarded as forming a metal–carbon σ-bond. In view of the low basicity of carbon monoxide, however, this is not in itself sufficient to explain the stability of the carbonyls, and a further source of bonding exists. In all of the metal carbonyls, there are filled non-bonding d-orbitals of the metal which are of the correct symmetry to overlap with fairly low-lying π-antibonding orbitals of carbon monoxide.

This formation of an additional π-bond by transference of charge from the metal can be seen to be, not only an additional bond, but also the means of strengthening the original σ-bond by removal of the unfavourable charge separation induced by the donor σ-bond. An improved σ-bonding is further seen to allow more extensive metal-to-ligand
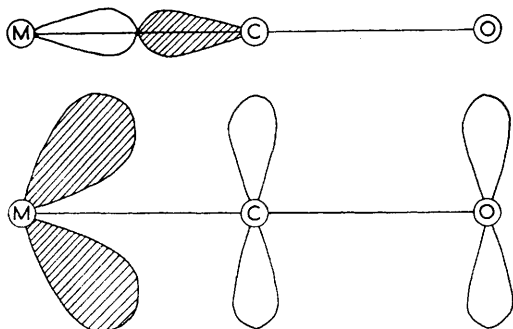

FIG. 2.   (a) *Formation of carbon–metal σ-bond.* (b) *Formation of metal–carbon π-bond.*

π-bonding. This produces what has been described[33b] as a "synergic" interaction between the two types of bonding, and this interaction probably accounts for a major part of the metal–carbon bond strength.

A major consequence of the presence of electrons in the π-antibonding orbital of carbon monoxide is the reduction in the order of the C–O bond. Whereas the C–O stretch frequency in carbon monoxide itself is about 2155 cm.$^{-1}$, the corresponding frequencies in terminal metal carbonyl groups lie at considerably lower values, and are usually around 2000 cm.$^{-1}$, though in certain special cases higher and lower frequencies are found.

In this scheme we see that the orders of the metal–carbon and carbon–oxygen bonds are roughly complementary, and any effect which increases

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[32] Gordy, Ring, and Burg, *Phys. Rev.*, 1950, **78**, 140.
[33] (a) Richardson, in "Organometallic Chemistry", ed. Zeiss, Reinhold, New York, 1960, p. 12; (b) Orgel, "An Introduction to Transition Metal Chemistry", Methuen and Co., London, 1960, p. 135.

one necessarily decreases the other. This point is well brought out in a consideration of the three species $Ni(CO)_4$, $[Co(CO)_4]^-$, and $[Fe(CO)_4]^{2-}$. These are isoelectronic and isostructural, but with a steadily increasing excess of negative charge. This charge will have the effect of increasing the extent of metal–carbon back-bonding, and hence raising the metal–carbon bond order. At the same time a corresponding fall-off in the carbon–oxygen bond order is to be expected.

TABLE 1. *Bond numbers for the species* $Ni(CO)_4$, $[Co(CO)_4]^-$, *and* $[Fe(CO)_4]^{2-}$.

	N_{C-O}	N_{M-C}	ΣN
$Ni(CO)_4$	2·64	1·33	3·97
$[Co(CO)_4]^-$	2·14	1·89	4·03
$[Fe(CO)_4]^{2-}$	1·85	2·16	4·01

In Table 1 is shown a set of self-consistent bond orders obtained[34] from spectroscopically derived force constants. Although these figures have been obtained by making many simplifications, and the slightly drastic assumption that stretching force constants are directly proportional to bond order, they do, nevertheless, indicate the reciprocal nature of the C–O and the M–C bond, by the close proximity of ΣN in each species to four. This effect might be described in Mulliken's classification[35] as "dative isovalent conjugation".

In addition to the linear M–C–O bond so far discussed, many metal carbonyl compounds contain carbon monoxide groups bonded to two or more metal atoms. It is notable that this "bridging" effect in carbonyl compounds is virtually confined to the derivatives of the first-row transition metals.
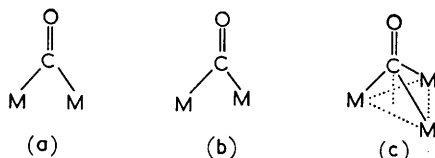

FIG. 3. (a) CO *bonded symmetrically to two metal atoms.* (b) CO *bonded asymmetrically to two metal atoms.* (c) CO *bonded to three metal atoms.*

As a simple picture it can be assumed that these bridging carbonyl groups contribute only one electron to each of the metal atoms, to form normal σ-bonds with metal electrons. The question of π-bonding in this case is more complicated, but it appears to be more extensive than, or of a different form to, that in terminal carbonyl groups.[36] This is deduced from the lowered carbon–oxygen bond order, as evidenced by CO stretching frequencies around 1850 cm.$^{-1}$. Although in most cases bridging carbonyl

[34] Stammreich, Kawai, Sala, and Krumholtz, *J. Chem. Phys.*, 1961, **35**, 2168.
[35] Mulliken, *Tetrahedron*, 1959, **5**, 253.
[36] Dunitz and Orgel, *J.*, 1953, 2594.

groups are symmetrically bound to two metal atoms, in the case of $(\pi\text{-}C_5H_5.Ni.CO)_2$ it is believed[37] that the carbonyl groups are asymmetrically disposed to the two nickel atoms as in Fig. 3 (b). Such groups would be part-way between a purely terminal carbonyl group and a purely bridging carbonyl group. A similar "partially bridging" carbonyl group has been observed[38] in the but-2-yne complex of iron carbonyl hydride, in which a M–C–O bond of 168° is present.

Carbon monoxide bonded simultaneously to three metal atoms [as in Fig. 3 (c)], has now been characterised[39] in $(\pi\text{-}C_5H_5.Ni)_3(CO)_2$; similar structures are thought to be present[38, 40] in the ions $[(\pi\text{-}C_6H_6.Co)_3(CO)_2]^+$ and $[Fe_3(CO)_{11}]^{2-}$. As might be expected, the CO stretching frequency in $(\pi\text{-}C_5H_5.Ni)_3(CO)_2$, where CO is bonded to three metal atoms, is at 1742 cm.$^{-1}$, even lower than that for CO bridging only two metal atoms.

(c) *The metal–metal bond.* The other important type of bond found in metal carbonyls is the metal–metal bond. This is often the only bond between two halves of a metal carbonyl or metal carbonyl derivative, as in $Mn_2(CO)_{10}$ and $(\pi\text{-}C_5H_5.Mo)_2(CO)_6$; or it may be present in conjunction with bridging carbonyl groups, as in $Fe_2(CO)_9$ and $(\pi\text{-}C_5H_5.Fe)_2(CO)_4$. When present with bridging carbonyl groups, the metal–metal bond is used to explain the diamagnetism of the binuclear species. It has been pointed out, however, that such resultant diamagnetism does not require a strong metal–metal bond, but only a relatively weak coupling of the unpaired spins, which could even come about through indirect interactions involving the carbonyl bridges.[33b] It is usual, however, to take the metal–metal distance in such compounds as suggesting a direct metal–metal bond.

Thus, for example, in $K_3W_2Cl_9$ the $[W_2Cl_9]^{3-}$ ion has W–Cl distances of 2·44 Å and a W–W distance of 2·41 Å, but in $Cs_3Cr_2Cl_9$ the Cr–Cr distance is 3·12 Å. It is concluded[41] from these metal–metal distances that, whereas a metal–metal bond is present in the ion $[W_2Cl_9]^{3-}$, no such bond exists in $[Cr_2Cl_9]^{3-}$.

(d) *The inert-gas rule.* With the exception of the recently discovered vanadium hexacarbonyl, all the binary metal carbonyls can be shown to obey what has come to be known as the "inert-gas rule". If we assume in the binary carbonyls that (a) terminal carbonyl groups each contribute a pair of electrons to the outer shell of the metal atom, (b) bridging carbonyl groups each contribute one electron to each of the metal atoms, and (c) covalent metal–metal bonds are formed by one electron from

[37] Palm, Doctorate Thesis, Munich 1959, quoted by Miller in "Advances in Inorganic and Radiochemistry", ed. Eméleus and Sharpe, Academic Press, New York, 1962, Vol. IV, p. 133.
[38] Mills, Hock, and Robinson, Abstract A, XVIIth Internat. Congress Pure Appl. Chem., Munich, 1959, p. 143.
[39] Mills in "Advances in the Chemistry of the Co-ordination Compounds", ed. Kirschner, Macmillan, New York, 1961, p. 640.
[40] Fischer and Beckert, *Angew. Chem.*, 1958, **70**, 744.
[41] Wells, "Structural Inorganic Chemistry", Oxford Univ. Press, 3rd edn., 1962.

each metal atom, then the total number of electrons available to the metal is equal to the number in the next-inert-gas shell. Carbon monoxide thus appears to differ considerably from other ligands, the majority of which readily form complexes in which unpaired electrons are present. Even the isoelectronic ligands CN^- and NO^+ form large numbers of compounds which do not obey any "inert-gas rule".[42]

It is difficult to explain why the metal carbonyls obey this rule. Possibly carbon monoxide forces the central atom in its complexes to have as many filled, formally non-bonding, electron pairs in the d-shell as possible, thus tending to improve the fulfilment of the requirements of π-bonding. Where formally one electron is likely to remain unpaired, the carbonyl derivative very frequently dimerizes with resulting spin-pairing of the odd electrons. Such pairing is remarkably shown in the series of carbonyl derivatives, $\pi\text{-}C_5H_5.V(CO)_4$, $[\pi\text{-}C_5H_5.Cr(CO)_3]_2$, $\pi\text{-}C_5H_5.Mn(CO)_3$, $[\pi\text{-}C_5H_5.Fe(CO)_2]_2$, $\pi\text{-}C_5H_5.Co(CO)_2$, and $[\pi\text{-}C_5H_5.Ni.CO]_2$, where any possibility of a metal atom's having a formally non-inert-gas configuration is counteracted by dimerization of every alternate member.

However, since the discovery of the paramagnetic vanadium hexa-carbonyl and many other paramagnetic metal carbonyl derivatives, it is becoming increasingly obvious that the closed metal shell for the carbonyls is not inviolable, though it is still a useful concept.

In some of the heavier-metal carbonyl derivatives, such as the carbonyl halides of platinum(II), palladium(II), and rhodium(I), the "closed shell" consists of 16 electrons only.

Physical Measurements on the Metal Carbonyls.—(a) *Thermodynamic and thermochemical measurements.* Numerous measurements of heats of combustion, formation, and sublimation have now been made for many of the metal carbonyls, but to date results are fragmentary and often discordant. The spontaneous decomposition of the metal carbonyls during the measurements has been a particular bar to great accuracy.

Perhaps of main interest have been the efforts to obtain values for the energy of the metal–carbon bond in the carbonyls. From direct measurements of heats of combustion, and the use of other available thermochemical data, we can obtain ΔH° for the process of converting one metal carbonyl bond into metal and carbon monoxide:

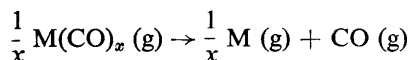$$\frac{1}{x} M(CO)_x \text{ (g)} \rightarrow \frac{1}{x} M \text{ (g)} + CO \text{ (g)}$$

Table 2 shows the values obtained[43, 44] for the different metal carbonyls examined.

[42] Griffith, *Quart. Rev.*, 1962, **16**, 188.
[43] Cotton, Fischer, and Wilkinson, *J. Amer. Chem. Soc.*, 1956, **78**, 5168; 1957, **79**, 2044.
[44] Cotton, Fischer, and Wilkinson, *J. Amer. Chem. Soc.*, 1959, **81**, 800.

TABLE 2. ΔH°_{298} for the reactions, $\dfrac{1}{x}$ M(CO)$_x$ (g) $\rightarrow$ $\dfrac{1}{x}$ M(g) + CO (g).

	Cr(CO)$_6$	Mo(CO)$_6$	W(CO)$_6$	Fe(CO)$_5$	Ni(CO)$_4$
ΔH°_{298} (kcal. mole^{-1})	27·1	35·9	42·1	27·7	35·2

It has been pointed out that the trend in the chemical stabilities of chromium, iron, and nickel carbonyls runs roughly in the opposite direction to that indicated by the values in Table 2, and is probably controlled by steric factors rather than by thermodynamic bond strengths.[44]

The values of bond energies given in Table 2 do, however, represent ΔH° for the metal–carbon bond with all species in their standard states. Perhaps a more "real" indication of metal–carbon bond energy is obtained as ΔH^* for the reaction:

$$\frac{1}{x}\text{ M(CO)}_x\text{ (g)} \rightarrow \frac{1}{x}\text{ M* (g)} + \text{CO (g)}$$
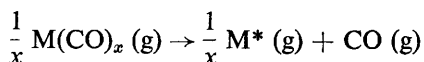
where M* (g) represents the metal in its "valency state". The promotion energies for $Cr(d^5s^1 \rightarrow d^6)$, $Fe(d^6s^2 \rightarrow d^8)$, and $Ni(d^8s^2 \rightarrow d^{10})$ are known, and if the necessary fraction ($1/x$) of these values is added to each of the values of ΔH° in Table 2, then the values of ΔH^* in Table 3 are obtained. No real significance can be attached to any trends in the values of ΔH^*, owing to the uncertainties in the procedure used for their determination. A value of about 85 kcal.mole^{-1} for the dissociation energy of the metal-carbon bond into valency states does, however, appear reasonable.[44]

TABLE 3. ΔH^* for the reactions, $\dfrac{1}{x}$ M(CO)$_x$ $\rightarrow$ $\dfrac{1}{x}$ M* (g) + CO (g).

	Cr(CO)$_6$	Fe(CO)$_5$	Ni(CO)$_4$
ΔH^* (kcal. mole^{-1})	87	89	77

By using the experimentally determined heat of sublimation, with other thermochemical data, and a spectroscopically derived valency-state promotion energy, an estimate has been made of ΔH for the process:

$$\text{Mn}_2\text{(CO)}_{10}\text{ (g)} \rightarrow 2\text{Mn(CO)}_5\text{ (g)}$$
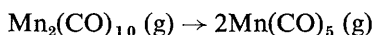
The value of 34 ± 13 kcal. mole^{-1} obtained for ΔH in this way gives, in effect, the energy of the metal–metal bond in manganese carbonyl. Most of the rather large uncertainty in this figure arises from the estimation of the promotion energy of manganese.[45] It has been observed that the Mn–Mn bond length (2·923 Å) in manganese carbonyl, as determined by X-rays, is 0·5 Å longer than that expected from the sum of the covalent radii.[46] Such a discrepancy from the "expected" metal–metal bond length

[45] Cotton and Monchamp, J., 1960, 533.
[46] Dahl, Ishishi, and Rundle, J. Chem. Phys., 1957, 26, 1750; Dahl and Rundle, Acta Cryst., 1963, 16, 419.

has also been observed[47] in $[\pi\text{-}C_5H_5.Mo(CO)_3]_2$. Cotton[45] thus questions the belief that a bond between such heavy atoms, which is 0·5 Å longer than it "should" be, could be as strong as 34 kcal. mole^{-1}. In the light of this, the values of the normal covalent radii assumed for zerovalent metals of the transitional groups are questionable.

In addition to the information on bond energies which has become available from thermodynamic data, it has been possible to throw some light on structural problems, and also to assess the validity of certain spectroscopic assignments.

From measurements of the heat capacity over the range 20—290°K, and the heats of fusion and vapourization of iron pentacarbonyl, the value of the standard entropy as an ideal gas has been found to be 106·4 ± 0·8 cal. mole^{-1} degree^{-1} at 25°/one atm. This has been compared with the statistical entropy of the carbonyl, calculated from spectroscopic data by the rigid rotator-harmonic oscillator approximation. The computation was carried out for the trigonal-bipyramidal (D_{3h}) and the square-pyramidal (C_{4v}) model of the pentacarbonyl.[48] The experimental value of the entropy was found to be in better agreement with the D_{3h} model, and this structure for iron pentacarbonyl was subsequently confirmed by X-ray examination.[49]

From measurements of the heat of sublimation in the range 70—110°, and other available thermodynamic data, the standard entropy of molybdenum hexacarbonyl, as a gas has been reported to be 118·0 cal. mole^{-1} degree^{-1} at 25°/one atm. Values of the entropy were calculated from the conflicting spectroscopic vibrational assignments in the literature. From a comparison of the experimental value and the various spectroscopic values, it has been possible to distinguish between acceptable and unacceptable assignments.[50]

(b) *Infrared spectra.* There is little doubt that nowadays the most extensively measured physical property of the metal carbonyls and their derivatives is the infrared absorption spectrum.[51]

From a knowledge of the shape of the molecule, it is possible to evaluate the symmetry properties, and so the normal modes of vibration to be expected. It should then be possible to make assignments of the observed spectra, and even to decide between the alternative structures proposed for a particular species. In practice, however, spectra are often very complicated, owing to mixing of vibrations of the same symmetry, and controversy frequently arises regarding the exact assignment of all observed bands.

Despite this difficulty a great deal of useful information can be obtained

[47] Wilson and Shoemaker, *J. Chem. Phys.*, 1957, **27**, 809.
[48] Leadbetter and Spice, *Canad. J. Chem.*, 1959, **37**, 1923.
[49] Hanson, *Acta Cryst.*, 1962, **15**, 930.
[50] Monchamp and Cotton, *J.*, 1960, 1438.
[51] Cotton, in "Modern Co-ordination Chemistry", ed. Lewis, and Wilkins, Interscience Publ., Inc., New York, 1960, p. 333.

from infrared spectra. In many cases a simplified approach has been adopted, only the C–O stretching modes being measured, as these are not likely to undergo strong mixing with other vibrations. After the necessary symmetry operations with respect to this mode have been carried out for a particular species, it is possible to determine the number of CO stretching frequencies which should be active in the infrared spectrum. When the two or more structures have different predicted numbers of active modes, a comparison of these with the observed spectrum often enables a particular structure to be selected. Elegant examples of this have been given[52, 53] for the various cis- and trans-forms now known for the di- and tetra-substituted hexacarbonyls of group VI. Some of the structures in these compounds, initially assigned from a consideration of the CO stretching vibrations, have been subsequently confirmed by X-rays.[53] The cis–trans-isomerization in solution has been observed for these compounds, and the rate of reaction followed by the changes in intensity of the C–O stretch bands of the two species.[53] This method of determining the rate of a reaction by following the disappearance of the C–O modes of the reactants has been used in kinetic studies of the replacement reactions in metal carbonyl halides.[54]

In addition to this interest in the number of active carbonyl stretching modes, considerable interest has been taken in the actual numerical values of the frequencies. These occur over the approximate range 2150—1650 cm.$^{-1}$ in the metal carbonyls and their derivatives. In the neutral binary carbonyls, the high frequencies (say 2050—1900 cm.$^{-1}$) are regarded as due to terminal carbonyl groups, and the lower frequencies (say 1900—1800 cm.$^{-1}$) as due to the bridging carbonyl groups. Even in this restricted class of compounds, however, the evidence of peaks in the region 1900—1800 cm.$^{-1}$ must be treated with reserve. This difficulty is exemplified by absorption in the region 1820—1860 cm.$^{-1}$ in $Fe_3(CO)_{12}$ in a solution spectrum,[55] and at 1875 cm.$^{-1}$ in a single-crystal spectrum.[56] These absorptions have been widely accepted as evidence for the presence of bridging carbonyl groups in the molecule. Subsequent workers, however, discussed the extremely low relative intensity of these absorptions and questioned their assignment as fundamental modes.[57] The complex of $Fe_3(CO)_{12}$ is not now believed to contain bridging carbonyl groups; it is likely that these absorptions here arise, therefore, as a result of some other crystalline interactions or Fermi resonance.[58]

In derivatives of the metal carbonyls, such a wide range of frequencies occurs that the separate assignment of terminal and bridging frequencies often becomes difficult.

[52] Chatt and Watson, J., 1961, 4980.
[53] Poilblanc and Bigorgne, Bull. Soc. chim. France, 1962, 1301.
[54] Angelici and Basolo, J. Amer. Chem. Soc., 1962, 83, 2495.
[55] Sheline, J. Amer. Chem. Soc., 1951, 73, 1615.
[56] Dahl and Rundle, J. Chem. Phys., 1957, 27, 323.
[57] Cotton and Wilkinson, J. Amer. Chem. Soc., 1957, 79, 752.
[58] Corey and Dahl, Inorg. Chem., 1962, 1, 521.

An often ignored hazard in the recording of the infrared spectra of metal carbonyls lies in the choice of solvent. It has been observed that appreciable solute–solvent interaction occurs, with considerable shifts of the observed carbonyl stretching modes.[59, 60] It is thus important that comparisons of frequencies between different species must be made with spectra obtained in the same solvent. Solution spectra, where obtainable, must also be regarded as superior to those obtained for mulls or halide discs.[61]

As already mentioned, the terminal carbonyl groups in neutral binary metal carbonyls absorb around 2000 cm.$^{-1}$. One of the strongest affects upon this frequency value is the presence of a charge on the species. In accordance with the mode of bonding in these compounds, positive charges are found to raise the C–O stretching frequency (by roughly 100 cm.$^{-1}$) and negative charges to lower them (also by roughly 100 cm.$^{-1}$). The isoelectronic and isostructural series in Table 4 well illustrate this point.

TABLE 4. C–O *stretching frequencies in the infrared spectra of some neutral carbonyls, carbonyl anions, and carbonyl cations.*

$[V(CO)_6]^-$	$[Cr(CO)_6]$	$[Mn(CO)_6]^+$	$[Fe(CO)_6]^{2+}$		
1859*	1981*	2090*	(?)		
	$[Cr(CO)_5]^{2-}$	$[Mn(CO)_5]^-$	$[Fe(CO)_5]$		
	(?)	1895†	2034†		
		1863	2014		
			$[Fe(CO)_4]^{2-}$	$[Co(CO)_4]^-$	$[Ni(CO)_4]$
			1786†	1886†	2057†
$[\pi\text{-}C_5H_5V(CO)_3]^{2-}$	$[\pi\text{-}C_5H_5Cr(CO)_3]^-$	$[\pi\text{-}C_5H_5Mn(CO)_3]$			
1748‡	1876‡	2035‡			
1645	1695	1935			

*Beck and Nitzchmann, *Z.Naturforsch.*, 1962, **17**b, 577.
†Edgell, Huff, Thomas, Lehmann, Angell, and Astata, *J. Amer. Chem. Soc.*, 1960, **82**, 1254.
‡Beck, *Chem. Ber.*, 1961, **94**, 1214.

This effect of charge upon the carbonyl stretching modes has now been very widely observed in all types of metal carbonyl derivative.

Another cause of lowered C–O frequencies is the presence in a substituted metal carbonyl of donating ligands, such as phosphines, amines, sulphides, ethers, etc. These would favour strong π-bonding between the metal and the remaining carbonyl groups in the molecule. A consequence of this would be a lowered C–O bond order and hence lowered C–O stretching frequency. This effect is shown for a selection of substituted metal carbonyls in Table 5.

[59] Barraclough, Lewis, and Nyholm, *J.*, 1961, 2582.
[60] Beck and Nitzchmann, *Z. Naturforsch.*, 1962, **17**b, 577; Bor, *Spectrochim. Acta*, 1962, **18**, 817.
[61] Orgel, *Inorg. Chem.*, 1962, **1**, 25.

TABLE 5. C–O *stretching frequencies in the infrared spectra of some substituted metal carbonyls.*

†digly.Mo(CO)$_3$^{a}	1905, 1835	*diars.Ni(CO)$_2$^{b}	1996, 1940
Me$_3$P.Ni(CO)$_3$^{c}	2063, 1989	PF$_3$.Ni(CO)$_3$^{c}	2109, 2047
cis-[Ph$_3$P]$_3$Mo(CO)$_3$^{d}	1934, 1835	*cis*-[PCl$_3$]$_3$Mo(CO)$_3$^{d}	2040, 1989
‡dien.Mo(CO)$_3$^{e}	1883, 1723	‡[dien.Mn(CO)$_3$]$^+$ I$^-$^{e}	2034, 1903

^{a} Werner and Coffield, *Chem. and Ind.*, 1960, 936. ^{b} Nyholm, *J.*, 1952, 2906. ^{c} Bigorne and Zelwer, *Bull. Soc. chim. France*, 1960, 1986. ^{d} Poilblanc and Bigorgne, *Bull. Soc. chim. France*, 1962, 1301. ^{e} Abel, Bennett, and Wilkinson, *J.*, 1959, 2323.

*diars = *o*-phenylenebisdimethylarsine. †digly = diethyleneglycol dimethyl ether. ‡dien. = diethylenetriamine.

It can be seen that a ligand such as diethylenetriamine (dien), which has no capacity for back-donation, produces very low values for CO stretch modes in dien.Mo(CO)$_3$. This strong flow of charge from metal to carbonyl in a dien complex can, however, be partly checked by the presence of an excess positive charge, as in the cation [dien.Mn(CO)$_3$]$^+$, whose C–O stretching frequencies are considerably higher than those of the isoelectronic dien.Mo(CO)$_3$.

A comparison of the carbonyl stretch modes of digly.Mo(CO)$_3$ and dien.Mo(CO)$_3$, however, indicates that the electronegativity of the donor atom is also an important factor.

Ligands which themselves have a capacity for π-bonding with a transitional metal do not in general produce such low frequencies as do the non-back-bonding ligand. A further secondary effect can be observed in the π-bonding ligands, where the groups attached to the ligand atom are important. Thus we see that phosphorus trichloride does not produce as large a drop in frequency as does triphenylphosphine. The chlorine atoms could decrease the strength of the P→M σ-bond by restricting the extent of donation, and also increase the strength of the P←M π-bond. Both of these effects would be expected to raise the C–O bond order in the remaining carbonyl groups. In the case of phosphorus trifluoride, the frequencies of the remaining carbonyl groups are higher than those of the parent carbonyl. This appears to indicate that in PF$_3$.Ni(CO)$_3$ the metal–carbon linkage is weaker than in Ni(CO)$_4$ itself, owing to the presence of the very powerfully π-bonding PF$_3$ ligand, which is itself able to form a complex Ni(PF$_3$)$_4$ analogous to nickel tetracarbonyl.[62]

The actual intensities of the absorption bands in the metal carbonyls and their derivatives have been little investigated. The integrated intensity per carbonyl group in a metal carbonyl compound is approximately 3—7 times higher than that of a saturated ketone. In general, it is also found that influences which lower the frequency raise the intensity, and *vice versa*, but that bridging carbonyl groups have both lower frequencies and lower specific intensities than have terminal carbonyl groups.[60, 63]

[62] Wilkinson, *J. Amer. Chem. Soc.*, 1951, **73**, 5501.
[63] Noack, *Helv. Chim. Acta*, 1962, **45**, 1847.

(c) *Raman spectra*. The Raman spectra of the metal carbonyls are difficult to obtain in many cases, as the low solubility of certain carbonyls makes shifts difficult to observe. Extensive photochemical decomposition has further obstructed measurements, but the use of carefully selected activating radiations and filters has now largely solved the problem of decomposition.[64]

Raman spectra have been used largely to complement infrared spectra, in order to observe vibrations which are not infrared-active, and particularly to detect the very low-frequency fundamentals not easily obtainable from infrared measurements.

Thirteen shifts ranging from 2114 to 68 cm.$^{-1}$ have been observed for iron pentacarbonyl. These are believed to be the thirteen fundamental modes expected from a D_{3h} structure of the molecule. These values, coupled with the available infrared data for the molecule, enable a complete assignment of all the vibrational modes to be made, and also enable us to adduce the trigonal-bipyramidal structure with reasonable certainty for this species.[65]

A band at 2017 cm.$^{-1}$ in the Raman spectrum of gaseous nickel carbonyl has been attributed[66] to the E vibration of ^{12}CO in the molecule $Ni(^{13}CO)(^{12}CO)_3$. Jones[67] has found a similar band at 2018 cm.$^{-1}$ in the infrared spectrum of the gaseous carbonyl but, whilst in agreement that the band is due to the $Ni(^{13}CO)(^{12}CO)_3$ species, prefers to assign it as the A_1 vibration of ^{13}CO. The observation of a band in this way resulting from the reduction of the T_d symmetry of $Ni(CO)_4$ to the C_{3v} symmetry of $Ni(^{13}CO)(^{12}CO)_3$ is particularly interesting. Although the natural abundance of ^{13}CO is only about 1% the abundance of $Ni(^{13}CO)(^{12}CO)_3$ in a bulk sample of nickel tetracarbonyl would be about 4% and in the hexacarbonyls the $M(^{13}CO)(^{12}CO)_5$ species with C_{4v} in place of the O_h symmetry of $M(^{12}CO)_6$, would represent approximately 6% of the molecules present. It is likely that other observations of a relaxation in the selection rules for infrared and Raman spectra, resulting from the presence of ^{13}CO in the metal carbonyls, should be possible.

(d) *Magnetic susceptibility*. The majority of metal carbonyls and metal carbonyl derivatives are diamagnetic, with fully paired electron systems. Magnetic-susceptibility measurements have shown in recent years, however, that a number of paramagnetic metal carbonyl derivatives exist (cf Table 6). Some of these paramagnetic species such as tricarbonyl-*o*-phenylenebisdimethylarsinemanganese exist in a monomeric paramagnetic form, and also a dimeric spin-paired form which is diamagnetic, the two forms being interconvertible.[68] Also some species such as tetracarbonyl(triphenyl phosphite)manganese, though diamagnetic

[64] Stammreich, *Spectrochim. Acta*, 1956, **8**, 41.
[65] Stammreich, Sala, and Tavares, *J. Chem. Phys.*, 1959, **30**, 856.
[66] Bigorgne and Chelkowski, *Compt. rend.*, 1960, **251**, 538.
[67] Jones, *J. Chem. Phys.*, 1955, **23**, 2448.
[68] Nyholm and Rao, *Proc. Chem. Soc.*, 1959, 130.

and dimeric in the solid state, dissociate in solution to produce the paramagnetic monomer.[69] It now seems likely that, provided steric and electronic conditions are so arranged, many other paramagnetic metal carbonyl compounds may be prepared.

TABLE 6.   *Some paramagnetic metal carbonyl species.*

V	VI	VII
$V(CO)_6{}^a$	$Cr(CO)_5I{}^b$	o-phen.$Mn(CO)_3{}^c$
		†diars.$Mn(CO)_3{}^d$
		$Ph_3P.Mn(CO)_4{}^e$
		$Et_3P.Mn(CO)_4{}^e$
		‡$[(PhO)_3P.Mn(CO)_4]_2{}^e$
		‡$[(C_6H_{11})_3P.Mn(CO_4]_2{}^e$

VIII

diars.$Fe(CO)_2I{}^f$	$[(\pi\text{-}C_6H_6.Co)_3(CO)_2]^{+g}$	$(\pi\text{-}C_5H_5.Ni)_3(CO)_2{}^h$

†Also exists as a diamagnetic dimer. o-phen = o-phenylenediamine.
‡Paramagnetic only upon dissociation.   diars   = o-phenylenebisdimethylarsine.
in solution.

^{a} Calderazzo, Cini, Corradini, Ercoli, and Natta, *Chem. and Ind.*, 1960, 500.
^{b} Behrens and Zizlsperger, *Z.Naturforsch.*, 1961, **16**b, 349.
^{c} Hieber and Schrop, *Z.Naturforsch.*, 1960, **15**b, 271.
^{d} Nyholm and Ramana Rao, *Proc. Chem. Soc.*, 1959, 130.
^{e} Hieber and Freyer, *Chem. Ber.*, 1959, **92**, 1765.
^{f} Nigam, Nyholm, and Ramana Rao, *J.*, 1959, 1397.
^{g} Fischer and Beckert, *Angew. Chem.*, 1958, **70**, 744.
^{h} Fischer and Palm, *Chem. Ber.*, 1958, **91**, 1725.

(*e*) *Nuclear magnetic resonance.* Measurements of nuclear magnetic resonance spectra have been widely carried out on the organic derivatives of metal carbonyls and on hydridocarbonylmetal species. These measurements have been in the main for proton[70] and fluorine shieldings.[71]

Observation of the ^{13}C resonance in iron pentacarbonyl led to the rather surprising observation of only one band, instead of the expected two with intensity ratio 3:2 for a D_{3h} configuration. Of the possible explanations for this, it is believed most likely that the chemical shift between the two carbonyl environments is smaller than the spectral resolution (~ 40 c./sec.) used in the observation.[72]

High-resolution ^{13}C and ^{17}O nuclear resonance spectra of $Fe(CO)_5$, $Ni(CO)_4$, and $Fe(CO)_2(NO)_2$ have been reported together with the ^{17}O spectra of $Mn_2(CO)_{10}$ and $Co(CO)_3(NO)$. The ^{13}C shifts, relative to benzene, lie in the range -64 to -84.6 p.p.m., and the ^{17}O shifts, relative to water, in the range -355 to -418 p.p.m. All of the compounds

[69] Hieber and Freyer, *Chem. Ber.*, 1959, **92**, 1765.
[70] Davison, McFarlane, Pratt, and Wilkinson, *J.*, 1962, 3653.
[71] Boston, Sharp, and Wilkinson, *J.*, 1962, 3488; King, Pitcher, Stafford, Treichel, and Stone, ref. 38, p. 619.
[72] Cotton, Danti, Waugh, and Fessenden, *J. Chem. Phys.*, 1958, **29**, 1427.

examined gave only single-line spectra, both of ^{13}C and ^{17}O. The small range of both the ^{13}C and the ^{17}O chemical shifts observed for these compounds appears to indicate that the bonding in the carbonyl group must be only little affected by the bond to the metal atom.

The absence of fine structure, which might be expected for some of these compounds, has been discussed, and the possibility of a ^{13}C chemical shift of only a fraction of 1 p.p.m. between the axial and the equatorial carbonyl groups in $Fe(CO)_5$ seems possible.[73] A belief that the observation of a nuclear magnetic resonance spectrum for vanadium hexacarbonyl was an indication of diamagnetism has been shown to be incorrect.[74]

(*f*) *Radioisotope-exchange studies.* Although not strictly a physical property of the carbonyls, the results obtained to date in radioisotope studies are conveniently included here. Relatively few measurements have been reported so far in this field, but those available are of considerable interest.[75] In solution, in the dark, the exchange of radiocarbon monoxide with chromium hexacarbonyl, manganese dodeca-carbonyl, or iron pentacarbonyl is very slow. It is moderately slow for vanadium hexacarbonyl, and very fast for cobalt octacarbonyl and nickel tetracarbonyl. The paramagnetic vanadium hexacarbonyl is probably a special case, as d^5 systems are generally more labile than d^6 systems, and also there are fewer electrons for metal-to-carbon π-bonding than in the hexa-carbonyls of group VI. The high reactivity of cobalt octacarbonyl may be due to a low-energy exchange path provided by the "hole" in the structure of the molecule (see below). In the exchange studies on $Co_2(CO)_8$, no distinc-tion was apparent, however, between the bridging and the non-bridging carbonyl groups. Except for these two special cases, the reactivity of the first-row carbonyls appears to depend upon co-ordination number. A similar trend has been observed in cyanide complexes.

Kinetic study of exchange in nickel carbonyl in toluene solution has shown a first-order rate constant of $7 \cdot 5 \times 10^{-4}$ sec.$^{-1}$, indicating an S_N1 process for the exchange:[76]

$$Ni(CO)_4 \rightleftharpoons Ni(CO)_3 + CO$$

This dissociative path is in accord with the results obtained both by flash-photolysis[77] and by thermal-decomposition studies.[78] The activation energy of this dissociative exchange reaction (13 kcal. mole^{-1}) is very considerably less than the mean nickel–carbon bond energy (estimated at 77 kcal.mole^{-1}). That the energy requirement for the fission of the first Ni–C bond is so very much less than the mean Ni–C bond energy,

[73] Bramley, Figgis, and Nyholm, *Trans. Faraday Soc.*, 1962, **58**, 1893.

[74] Calderazzo, Cini, Corradini, Ercoli, and Natta, *Chem. and Ind.*, 1960, 500.

[75] Basolo and Pearson, in "Advanced in Inorganic and Radiochemistry", ed. Emeléus and Sharpe, Academic Press, New York, 1961, Vol. III, p. 68.

[76] Basolo and Wojcicki, *J. Amer. Chem. Soc.*, 1961, **83**, 520.

[77] Callear, *Proc. Roy. Soc.*, 1961, *A*, **265**, 71.

[78] Garratt and Thompson, *J.*, 1934, 1817, 1822; Bawn, *Trans. Faraday Soc.*, 1935, **31**, 440.

may be explicable in terms of the stabilization effect of π-bonding in the planar sp^2 transition state. The π-bonding could possibly be more effective in the transition state than in the tetracarbonyl itself.[75,79]

The incorporation of labelled carbon monoxide into iron enneacarbonyl during the photochemical decomposition of iron pentacarbonyl in the presence of radiocarbon monoxide was very small. This suggests that a photodissociation process is not a major reaction path. A possible path not involving photodissociation is believed to require an activated iron pentacarbonyl species:

$$Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_5{}^*$$
$$Fe(CO)_5 + Fe(CO)_5{}^* \to Fe_2(CO)_9 + CO \uparrow$$
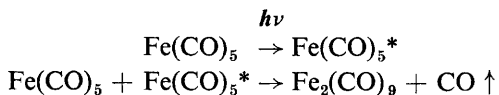
It is apparent that such a process would not introduce ^{14}CO into the product.[80]

Exchange studies[81] with the manganese pentacarbonyl halides are in agreement with the experimental observations[82] that there are four reactive carbonyl groups in these compounds, and one less active. A possible explanation for this is that the Mn–C bond in the position *trans* to the halide atom is stronger than the Mn–C bond *trans* to other carbonyl groups, a result of ligands in these d^6 systems competing for the same sets of d_{xy}, d_{xz}, and d_{yz} orbitals for π-bonding.

The rates of carbon monoxide exchange in these manganese carbonyl halides do not depend upon concentration of radiocarbon monoxide; thus an S_N1 reaction is indicated. Any five co-ordinate, active intermediate must from the above arguments retain the identity of the one inactive carbonyl group. Both trigonal-bipyramidal or square-pyramidal intermediates can be postulated.[81] A final point of interest in the exchange studies on these manganese pentacarbonyl halides is the ratio of the rates of exchange for the three halides, $I:Br:Cl = 1:8:200$. Since I^- has the greatest polarizability and the lowest electronegativity it renders the manganese least positive, and hence allows strongest metal-to-carbon π-bonding with the consequent lowest rate of exchange.

By analogy with these results, the iron compound $Fe(CO)_4I_2$ might be expected to have only two reactive carbonyl groups. In complete contrast to the manganese compounds, however, all four carbonyl groups undergo exchange at the same rate, but by a S_N2 process.[81] This may be the result of a nucleophilic attack promoted by the greater positive charge on the iron atom. For a bimolecular process an intermediate $Fe(CO)_4(^{14}CO)I_2$ would be required, and it is of interest that the species $Fe(CO)_5I_2$ has been isolated at low temperature after reaction between iodine and iron

[79] Kimball, *J. Chem. Phys.*, 1940, **8**, 188.
[80] Keeley and Johnson, *J. Inorg. Nuclear Chem.*, 1959, **11**, 33.
[81] Wojcicki and Basolo, *J. Amer. Chem. Soc.*, 1961, **83**, 525.
[82] Abel and Wilkinson, *J.*, 1959, 1501; Angelici, Basolo, and Poë, *Nature*, 1962, **195**, 993; Gray, Bernal, and Billig, *J. Amer. Chem. Soc.*, 1962, **84**, 3404.

pentacarbonyl.[83] The structure of the compound $Fe(CO)_5I_2$ is, however, not yet known.

Specific Binary Metal Carbonyl Systems.—The known neutral binary metal carbonyls and binary carbonyl anions and cations are summarized in Table 7.

Vanadium group. This is the lowest group in the Periodic Table in which simple binary metal carbonyl species have been reported, although a titanium carbonyl compound $(\pi\text{-}C_5H_5)_2Ti(CO)_2$ is known in group IV.[84]

To date, vanadium hexacarbonyl is the only example of a paramagnetic binary carbonyl.[73, 74] As it is one electron short of a complete inert-gas shell, it is not surprising that vanadium hexacarbonyl is considerably less stable than the hexacarbonyl of chromium, molybdenum, and tungsten. The diamagnetic ion $[V(CO)_6]^-$, however, is isoelectronic with the group VI hexacarbonyls, and it is notably more stable than the paramagnetic neutral carbonyl.[85,86]

The anions $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ have both been reported, but neutral carbonyls of niobium and tantalum are not yet known.[87]

TABLE 7.   *The binary neutral metal carbonyls and binary metal carbonyl anions and cations.*

$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_4$
$[V(CO)_6]^-$	$[Cr(CO)_5]^{2-}$	$[Mn(CO)_5]^-$	$Fe_2(CO)_9$	$Co_4(CO)_{12}$	$[Ni_2(CO)_6]^{2-}$
	$[Cr_2(CO)_{10}]^{2-}$	$[Mn(CO)_6]^+$	$Fe_3(CO)_{12}$	$[Co(CO)_4]^-$	$[Ni_4(CO)_9]^{2-}$
	$[Cr_3(CO)_{14}]^{2-}$		$[Fe(CO)_4]^{2-}$		
			$[Fe_2(CO)_8]^{2-}$		
			$[Fe_3(CO)_{11}]^{2-}$		
			$[Fe_4(CO)_{13}]^{2-}$		
			$[Fe(CO)_6]^{2+}$		
$[Nb(CO)_6]^-$	$Mo(CO)_6$	$Tc_2(CO)_{10}$	$Ru(CO)_5$	$Rh_2(CO)_8$	
	$[Mo(CO)_5]^{2-}$		$Ru_3(CO)_{12}$	$[Rh(CO)_3]_{4(?)}$	
	$[Mo_2(CO)_{10}]^{2-}$			$Rh_4(CO)_{11}$	
	$[Mo_3(CO)_{14}]^{2-}$				
$[Ta(CO)_6]^-$	$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$	$Ir_2(CO)_8$	
	$[W(CO)_5]^{2-}$	$[Re(CO)_5]^-$	$Os_3(CO)_{12}$	$[Ir(CO)_3]_{4(?)}$	
	$[W_2(CO)_{10}]^{2-}$	$[Re(CO)_6]^+$	$[Os(CO)_6]^{2+}$		

Chromium group. The hexacarbonyls of chromium, molybdenum, and tungsten are now very well known, and infrared, Raman, electron diffraction, and *X*-ray measurements are in agreement with a perfectly octahedral structure for these compounds. Very large numbers of substituted carbonyls are known for this group where carbonyl groups

[83] Hieber and Bader, *Ber.*, 1928, **61**, 1717.
[84] Murray, *J. Amer. Chem. Soc.*, 1959, **81**, 752; 1961, **83**, 1287.
[85] Hieber, Peterhans, and Winter, *Chem. Ber.*, 1961, **94**, 2572.
[86] Werner, *Z. Naturforsch.*, 1961, **16**b, 477.
[87] Werner and Podall, *Chem. and Ind.*, 1961, 144.

have been partly replaced, either by various ligands in which the donor atom is oxygen,[88] sulphur,[89] nitrogen,[13] phosphorus,[13] arsenic,[13] or halogen,[90] etc., or by an unsaturated hydrocarbon ligand.[14–17]

An unstable pentacarbonyl of tungsten has been isolated from the low-temperature irradiation of tungsten hexacarbonyl. The compound $W(CO)_5$ has a half-life of two minutes at room temperature and is believed to have a square-pyramidal structure. Electron spin resonance studies show no evidence for the existence of unpaired electrons in the species.[91] The existence of neutral pentacarbonyls of group VI as reaction intermediates had been previously postulated.[62, 92]

In addition to these neutral carbonyls, many metal carbonyl anions have been reported in this group. The ions $[M(CO)_5]^{2-}$ (M = Cr, Mo, or W) are produced[93] as sodium salts by the action of metallic sodium on the hexacarbonyls in liquid ammonia. In the absence of evidence to the contrary, it is reasonable to suggest that these ions might have a trigonal-bipyramidal configuration; thus $[Cr(CO)_5]^{2-}$ would be both isoelectronic and isostructural with iron pentacarbonyl.

Reduction of the hexacarbonyls with sodium borohydride in liquid ammonia gives[94] the anions $[M_2(CO)_{10}]^{2-}$ (M = Cr, Mo, or W). The structure of these ions is likely to be the same as that of the neutral $M_2(CO)_{10}$ carbonyls of group VII, with which they are isoelectronic. This is supported by the very close similarities of the infrared spectra[95] in the carbonyl stretching region:

$$\begin{cases} [Cr_2(CO)_{10}]^{2-} \\ Mn_2(CO)_{10} \end{cases}$$ 1945, 1922, and 1897 cm.$^{-1}$
2074, 2015, and 1972 cm.$^{-1}$

$$\begin{cases} [W_2(CO)_{10}]^{2-} \\ Re_2(CO)_{10} \end{cases}$$ 1944, 1906, and 1889 cm.$^{-1}$
2049, 2013, and 1983 cm.$^{-1}$

The profiles of the spectra are very similar, and the shifts of approximately 100 cm.$^{-1}$ for each absorbance maximum in going from neutral carbonyl to the anionic species is that expected from the improved metal-to-carbon π-bonding in the presence of an excess of negative charge.

Sodium borohydride in tetrahydrofuran reacted with the hexacarbonyls of chromium and molybdenum, to produce[96] the trimeric anions

[88] Werner and Coffield, ref. 38, p. 534; Chem. and Ind., 1960, 936.
[89] Cotton and Zingales, Inorg. Chem., 1962, 1, 145; Mannerskantz and Wilkinson, J., 1962, 4454.
[90] Fischer and Öfele, Chem. Ber., 1960, 93, 1156; Abel, Bennett, and Wilkinson, Chem. and Ind., 1960, 442.
[91] Stolz, Dobson, and Sheline, J. Amer. Chem. Soc., 1962, 84, 3589.
[92] Strohmeier, Chem. Ber., 1961, 94, 3337.
[93] Behrens and Weber, Z. anorg. Chem., 1955, 291, 122; Behrens and Klek, ibid., 1957, 292, 151; Behrens and Kohler, Z. Naturforsch., 1959, 14b, 463; Behrens and Haag, ibid., 1959, 14b, 600.
[94] Behrens and Haag, Chem. Ber., 1961, 94, 312.
[95] Hieber, Beck, and Braun, Angew. Chem., 1960, 72, 795.
[96] Behrens and Haag, Chem. Ber., 1961, 94, 320.

$[M_3(CO)_{14})]^{2-}$. No physical data or structural information are available for these ions, but it is possible that two metal–metal bonds are present to give a linear structure $[(CO)_5M.M(CO)_4.M(CO)_5]^{2-}$, in which each metal atom is essentially in an octahedral environment. The ions can undergo interconversion reactions:

$$[M_3(CO)_{14}]^{2-} + 2CO \rightarrow [M_2(CO)_{10}]^{2-} + M(CO)_6$$
$$[M_2(CO)_{10}]^{2-} + CO \rightarrow [M(CO)_5]^{2-} + M(CO)_6$$
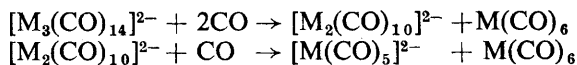
Manganese group. Metal carbonyls of formula $M_2(CO)_{10}$ are known for manganese, technetium,[97] and rhenium. Structurally they are of interest, in that they contain two square-pyramidal $M(CO)_5$ groups joined solely by a metal–metal bond, giving each metal atom, in effect, octahedral co-ordination.
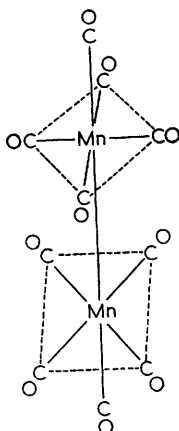
FIG. 4.   *Structure of manganese carbonyl.*

A detailed X-ray structural investigation of crystalline manganese carbonyl gives the result[46] shown in Fig. 4. Two sets of four equatorial carbonyl groups are arranged in a staggered configuration with the remaining two carbonyl groups axial. The carbonyl groups in the equatorial planes are bent slightly towards the other half of the molecule. This places the manganese atoms 0.12 Å out of the equatorial planes of carbon atoms. It is suggested[46] that this distortion is due to crystal packing, but it would nevertheless be particularly interesting to have accurate interatomic distances for this molecule in the gas phase and in solution.

Many methods have been reported[98–100] for the formation of the

[97] Hileman, Huggins, and Kaesz, *J. Amer. Chem. Soc.*, 1961, **83**, 2953; Hieber and Herget, *Angew. Chem.*, 1961, **73**, 579; Walloch, *Acta Cryst.*, 1962, **15**, 1058.
[98] Coffield, Kozikowski, and Closson, *J. Org. Chem.*, 1957, **22**, 598.
[99] Hieber and Wagner, *Z. Naturforsch.*, 1957, **12b**, 478; 1958, **13b**, 339.
[100] Hieber and Schropp, *Z. Naturforsch*, 1960, **15b**, 271; *Chem. Ber.*, 1960, **93**, 455.

$[Mn(CO)_5]^-$ ion. Perhaps the simplest is the direct formation of the sodium salt with metallic sodium:[98]

$$Mn_2(CO)_{10} + 2Na \rightarrow 2Na^+[Mn(CO)_5]^-$$
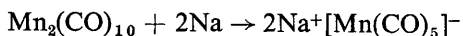
From a study of the infrared spectrum of the pentacarbonylmanganate ion, it is believed to have a trigonal-bipyramidal structure.[101] Rhenium forms a similar ion $[Re(CO)_5]^-$, and the anions $[Re_2(CO)_9]^{2-}$ and $[Mn_2(CO)_9]^{2-}$ have been mentioned as reaction intermediates.[102]

Manganese pentacarbonyl chloride reacts with carbon monoxide in the presence of aluminium chloride to produce the manganese hexacarbonyl cation:[103]

$$Mn(CO)_5Cl + CO + AlCl_3 \rightarrow [Mn(CO)_6]^+(AlCl_4)^-$$
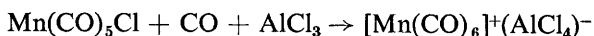
This cation is isoelectronic with chromium hexacarbonyl, and is presumably perfectly octahedral in structure. The analogous hexacarbonyl of rhenium, $[Re(CO)_6]^+$, has also been prepared in a similar manner.[104]

Iron group. The structure of the iron pentacarbonyl molecule has been controversial for some time. Combined infrared and Raman spectral measurements had presented fairly conclusive evidence for a trigonal-bipyramidal structure.[65] Thermodynamic measurements[48] and, more recently, values of the dielectric constant at microwave frequencies[105] supported this assignment, and it has now been fully confirmed by a single-crystal X-ray determination at low temperature.[49]

In the crystal, some distortion from an ideal trigonal bipyramid is observed, oxygen atoms being displaced by up to 0·13 Å, and this is believed to allow a closer packing in the crystal.

Ruthenium and osmium form pentacarbonyls,[11] both of which are much less stable than iron pentacarbonyl, in line with a decreased tendency towards five co-ordination in the second- and third-row transitional series. These are likely to have the same structure as iron pentacarbonyl.

When iron pentacarbonyl is exposed to ultraviolet light, carbon monoxide is evolved, and dark yellow platelets of iron enneacarbonyl $Fe_2(CO)_9$ are deposited. An X-ray determination[106] of this compound gave the structure shown in Fig. 5. Features of this structure are the terminal and bridging carbonyl groups, and the metal–metal bond. The character of the metal–metal bond is, however, vague, and it has been pointed out that the diamagnetism of this compound can be explained by a relatively weak coupling of the unpaired spins in some way.[36]

Iron enneacarbonyl was believed to be a member of the series $Fe_2(CO)_9$, $Ru_2(CO)_9$, and $Os_2(CO)_9$. It now appears that the enneacarbonyls of

[101] Wilson, *Z. Naturforsch.*, 1958, **13b**, 349.
[102] Beck, Hieber, and Braun, *Z. anorg. Chem.*, 1961, **308**, 23.
[103] Fischer and Öfele, *Angew. Chem.*, 1961, **73**, 581.
[104] Hieber and Kruh, *Angew. Chem.*, 1961, **73**, 580.
[105] Horrocks and Di Carlo, *J. Phys. Chem.* 1962, **66**, 186.
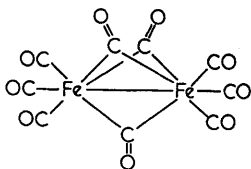[106] Powell and Ewens, *J.*, 1939, 286.

FIG. 5.   *Structure of iron enneacarbonyl reported from X-ray measurements.*

ruthenium[107] and osmium,[108] although reported as such, were incorrectly formulated.[109] This makes iron enneacarbonyl unique. The complete insolubility and non-volatility of this compound, when compared with all the other neutral carbonyls, are very difficult to explain on the basis of the presently accepted structure. Comparatively little is known of the physical and chemical properties of $Fe_2(CO)_9$, and further investigations appear necessary, in order to examine the possibility of some type of polymeric structure.

Many reactions of carbonylferrate anions and hydridocarbonyliron produce [11, 13] iron dodecacarbonyl, $Fe_3(CO)_{12}$. The structure of this species is not known with certainty, and has been the subject of numerous proposals.[110] That absorption in the region 1820—1860 cm.$^{-1}$ in the infrared spectrum was evidence of bridging carbonyl groups has been questioned;[57] it now appears likely that none is present. An *X*-ray study of iron dodecacarbonyl has shown[56] the iron atoms to be arranged at the corners of an equilateral triangle (Fe–Fe distance 2·75 Å), but a detailed analysis of the carbonyl positions in the molecule has been prevented by disordering of the molecules in the crystal. This triangular structure appears to rule out the linear structures previously proposed, and it now seems likely that iron dodecacarbonyl consists of three $Fe(CO)_4$ groups joined solely by metal–metal bonds. This D_{3h} structure has been conclusively shown[58] to be present in the analogous osmium dodecacarbonyl (Fig. 6).
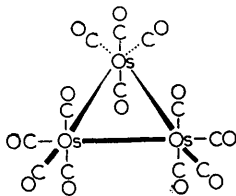

FIG. 6.   *Structure of osmium dodecacarbonyl.*

To a first approximation the metal–metal bonding of a structure such as that in Fig. 6 can be rationalized in terms of the overlap of octahedral-type metal orbitals, which in the molecule do not point directly at one

[107] Manchot and Manchot, *Z. anorg. Chem.*, 1936, **226**, 385.
[108] Hieber and Stallmann, *Z. Elektrochem.*, 1943, **49**, 288.
[109] Corey and Dahl, *J. Amer. Chem. Soc.*, 1961, **83**, 2203.
[110] Brown, *J. Inorg. Nuclear Chem.*, 1958, **5**, 289.

another. Such a metal–metal bond would involve non-axially symmetric electron-pair charge distribution between the metals. Such a "bent" metal–metal bond has been formulated[111] from molecular-orbital theory for the case of $Co_2(CO)_6(Ph \cdot C \vdots C \cdot Ph)$ and is also compatible with the structure of cobalt octacarbonyl. Similar triangular arrangements of metal atoms are now known in a number of metal carbonyl derivatives (see ref. [57]). The diamagnetism and also the infrared spectrum of osmium dodecacarbonyl are both reported [112] to be compatible with the structure found by X-rays.

A tetra-co-ordinated iron carbonyl is believed to have been formed by irradiation of iron pentacarbonyl.[91] The very low carbonyl stretch mode (1834 cm.$^{-1}$) reported for this species, however, makes it unlikely that it is a neutral $Fe(CO)_4$ compound.

Although not strictly a binary metal carbonyl, the iron carbonyl carbide, $Fe_5(CO)_{15}C$, is sufficiently similar in many features to the polynuclear carbonyls to merit mention here. The compound is formed in small quantities by the action of certain alkynes on iron dodecacarbonyl. Magnetic-susceptibility measurements have shown it to be diamagnetic, and it is free from bridging carbonyl groups.

The molecular configuration (Fig. 7) is found by X-rays to consist of an approximately equilateral tetragonal pyramid of iron atoms with only
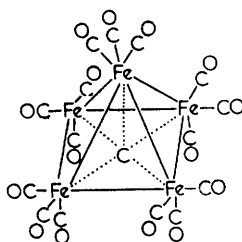

FIG. 7.   *Structure of* $Fe_5(CO)_{15}C$.

terminal carbonyl groups attached to each iron atom.[113] A completely new structural feature is the presence of a penta-co-ordinated carbon atom, just below the centre of the basal plane of iron atoms, at approximately equal distances from all five iron atoms. The presence of this carbon atom allows all five of the iron atoms to attain a closed shell structure in the ground state. A qualitative molecular-orbital description of the bonding in this system has been given.[113]

Various anionic carbonyls have been reported for iron. From the action of the necessary stoicheiometric equivalents of alkali and iron carbonyls, the salts $K_2Fe(CO)_4$, $K_2Fe_2(CO)_8$, and $K_2Fe_3(CO)_{11}$ are

[111] Brown, *J. Chem. Phys.*, 1960, **33**, 1037.
[112] Beck and Lottes, *Chem. Ber.*, 1961, **94**, 2578.
[113] Braye, Dahl, Hubel, and Wampler, *J. Amer. Chem. Soc.*, 1962, **84**, 4633.

reported.[114] The anions of each of these have also been prepared by other methods.[115,116]. A further anion $[Fe_4(CO)_{13}]^{2-}$ has been recorded from the interaction of pyridine and other organic bases with iron penta-carbonyl:[117]

$$5Fe(CO)_5 + 6py \rightarrow [Fe\,py_6]^{2+}[Fe_4(CO)_{13}]^{2-} + 12CO \uparrow .$$
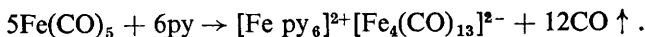
It is suggested that the $[Fe_4(CO)_{13}]^{2-}$ anion may be derived from an, as yet, unknown polynuclear carbonyl, $Fe_4(CO)_{14}$.

The inter-relationship of the carbonyl anions of iron has been studied and found to be more complex than previously realised. Interchanges have been shown to depend upon a number of factors including pH and temperature.[118]

The $[Fe(CO)_4]^{2-}$ ion is isoelectronic and isostructural with nickel tetracarbonyl. The $[Fe_2(CO)_8]^{2-}$ ion is believed[119] to have the structure shown in Fig. 8 (a). This configuration of $[Fe_2(CO)_8]^{2-}$ is in marked contrast with that of the isoelectronic cobalt octacarbonyl which contains bridging carbonyl groups in addition to a metal–metal bond.

Preliminary X-ray measurements[38] on the ion $[Fe_3(CO)_{11}]^{2-}$ suggest the structure shown in Fig. 8 (b). This remarkable mode of bonding,

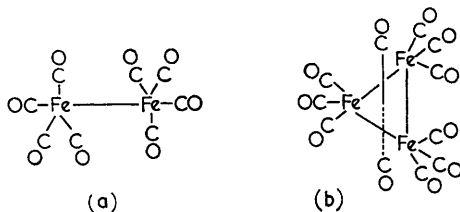Fig. 8.   *Suggested structures of* (a) $[Fe_2(CO)_8]^{2-}$ *and* (b) $[Fe_3(CO)_{11}]^{2-}$.

with two of the carbonyl groups each apparently situated equidistant from three metal atoms, has been confirmed for dicarbonytricyclopenta-dienyltrinickel.[39]

The metal carbonyl cation $[Fe(CO)_6]^{2+}$ has been suggested as an intermediate in some reactions of iron pentacarbonyl in which a self-ionization mechanism is proposed:

$$2Fe(CO)_5 \rightarrow [Fe(CO)_6]^{2+} + [Fe(CO)_4]^{2-}$$
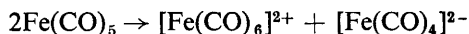
It is unlikely, however, that the carbonyl stretching frequency in the infrared spectrum, of 2016 cm.$^{-1}$, which has been assigned[120] to ·this

[114] Hieber and Leutert, *Z. anorg. Chem.*, 1932, **145**, 204; Hieber and Brendel, *ibid.*, 1957, **289**, 324.
[115] Hieber, Sedlmeier, and Werner, *Chem. Ber.*, 1957, **90**, 278.
[116] Behrens, *Z. Naturforsch.*, 1952, 7b, 321; Behrens and Weber, *Z. anorg. Chem.*, 1955, **281**, 190.
[117] Hieber and Werner, *Chem. Ber.*, 1957, **90**, 286.
[118] Case and Whiting, *J.*, 1960, 4632.
[119] Mills, quoted by Nyholm, Tilden Lecture, *Proc. Chem. Soc.*, 1961, 273.
[120] Sternberg, Friedel, Shufler, and Wender, *J. Amer. Chem. Soc.*, 1955, **77**, 2675.

species, is correct. The $[Fe(CO)_6]^{2+}$ ion would be expected to have a carbonyl stretching mode of about 2150 cm.$^{-1}$, resulting from the presence of the large excess of positive charge. $[Fe(CO)_6]^{2+}$ and $[Os(CO)_6]^{2+}$ have now both been reported,[104] but without details, and are probably made by methods analogous to those used[103, 104] for $[Mn(CO)_6]^+$ and $[Re(CO)_6]^+$.

Cobalt group. The two neutral carbonyls of cobalt are $Co_2(CO)_8$ and $Co_4(CO)_{12}$. In cobalt octacarbonyl [Fig. 9 (a)], each of the cobalt atoms
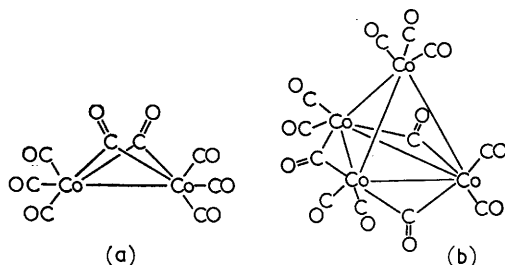

FIG. 9.   *The structures of* (a) *cobalt octacarbonyl and* (b) *cobalt dodecacarbonyl.*

may be effectively regarded as being in a distorted octahedral environment, from which one ligand is "missing".[121, 122]

It has been observed that, under high pressure, cobalt octacarbonyl takes up one molecule of carbon monoxide reversibly.[123] It is possible that this extra ligand is bonded weakly to both the cobalt atoms in the "hole" in the molecule, which thus becomes analogous in structure to iron enneacarbonyl. Also possible, however, is formation of the unstable salt $[Co(CO)_5]^+[Co(CO)_4]^-$.

In the phosphine-substituted cobalt carbonyl, $[Ph_3P.Co(CO)_3]_2$, there are no carbonyl stretching modes in the infrared spectrum[124] below 1900 cm.$^{-1}$. It therefore appears likely that in undergoing replacement in this way cobalt carbonyl has changed its mode of bonding to include only terminal carbonyl groups and probably a metal–metal bond. The reasons for such a delicate balance between terminal and bridging carbonyl groups is not as yet understood. A similar situation occurs with the compounds $(\pi\text{-}C_5H_5.Fe(CO)_2]_2$ and $[\pi\text{-}C_5H_5.Mo(CO)_3]_2$; in the former, bridging carbonyl groups are present, but in the latter only a single metal–metal bond holds the two halves of the molecule together.[125]

The high-resolution infrared spectrum of cobalt dodecacarbonyl has been found[126] to be considerably simpler than would be expected from the structure [Fig. 9 (b)], as determined by X-rays.[127] This presents a

[121] Sumner and Klug, *Acta Cryst.,* 1963, in press.
[122] Mills and Robinson, *Proc. Chem. Soc.,* 1959, 156.
[123] Metlin, Wender, and Sternberg, *Nature,* 1959, **183,** 457.
[124] Vohler, *Chem. Ber.,* 1958, **91,** 1235.
[125] See ref. 15, p. 47.
[126] Cotton and Monchamp, *J.,* 1960, 1882.
[127] Corradini *J. Chem. Phys.* 1959, **31,** 1676.

striking example of how a failure to observe as many infrared absorptions as are in principle required for a particular model is not conclusive evidence against such a model.

Rhodium and iridium also form carbonyls of the type $M_2(CO)_8$, and the carbonyls $[Rh(CO)_3]_x$ and $[Ir(CO)_3]_x$ are likely to be analogous to $Co_4(CO)_{12}$. The compound $Rh_4(CO)_{11}$ appears to be a definite crystalline species, but its structure, at present under investigation, is not yet known.[128]

The cobalt tetracarbonyl anion is often formed in the reactions of $Co_2(CO)_8$ and $Co_4(CO)_{12}$. The reaction $Co_2(CO)_8 + 2e \rightarrow 2Co(CO)_4{}^-$ has a redox potential of 0·4 volt.[129]

Many organic bases (B) react with cobalt octacarbonyl, to give carbon monoxide and products of the type $(CoB_6)^{2+}[Co(CO)_4{}^-]_2$. This is a general reaction for many carbonyls.[130] In some cases, instead of evolution of carbon monoxide, the formation of amides is reported by carbonylation of the excess of amine present.[131] These reactions have been postulated[132,133] as going initially *via* an ionization:

$$B + Co_2(CO)_8 \rightarrow [BCo(CO)_4]^+ + [Co(CO)_4]^-$$
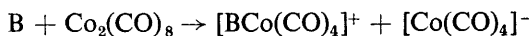
In cases where the base B is piperidine or dimethylamine, evidence for the formation of a $[BCo(CO)_4]^+$ species has been reported.

Nickel group. The only neutral carbonyl in this group is nickel tetracarbonyl. Although palladium and platinum both form carbonyl halides, and platinum the substituted[134] carbonyls $(R_3P)_2Pt(CO)_2$ and $(R_3P)_3PtCO$, no simple binary carbonyls have been isolated for these metals to date. Reasons for this have been discussed[135] in the light of the heats of atomization, spin-pairing promotion energies, and ionization potentials of the spin-paired states of the three metals in this group. Although the many different energies involved present a complicated picture, the major difference between nickel and the other two metals lies in the ionization potentials ($d^{10} \rightarrow d^9$) of the spin-paired states (Ni, 4·38; Pd, 8·33; Pt, 8·2 ev). These values can be taken as an indication of the ease with which metal-to-ligand back-bonding would take place from the d^{10} metal orbitals, and they are seen to favour greatly the stability of nickel tetracarbonyl in comparison with palladium or platinum tetracarbonyl. The formation of compounds of the type $(R_3P)_2Pt(CO)_2$ is explained by an increase in the limited donor capacity of platinum arising because the metal becomes more negatively charged in the presence of the phosphine ligands.

[128] L. F. Dahl, personal communication.
[129] Hieber and Hübel, *Z. Elektrochem.*, 1953, **57**, 331.
[130] Hieber, Beck, and Zeitler, *Angew. Chem.*, 1961, **73**, 364.
[131] Bird, *Chem. Rev.*, 1962, **62**, 283.
[132] Wender, Sternberg, and Orchin, *J. Amer. Chem. Soc.*, 1952, **74**, 1216.
[133] Sternberg, Wender, Friedel, and Orchin, *J. Amer. Chem. Soc.*, 1953, **75**, 3148.
[134] Malatesta and Corriello, *J.*, 1958, 2323.
[135] Nyholm, Tilden Lecture, *Proc. Chem. Soc.*, 1961, 273.

Nickel tetracarbonyl has been found to have a perfectly tetrahedral structure, from X-ray, infrared, Raman, and electron-diffraction measurements.

In addition to the neutral tetracarbonyl of nickel, complex binary anions are known. Salts of $[Ni_2(CO)_6]^{2-}$ and $[Ni_4(CO)_9]^{2-}$ have been prepared,[136] but the structures of these ions are not known. The hydride $Ni_2(CO)_6H_2$ corresponding to the hexacarbonyldinickelate ion has also been reported.[137]

Mixed metal carbonyls. Numerous metal carbonyl compounds are known in which more than one metal atom is present. The simplest type includes salts such as $Na_2[Cr(CO)_5]$, $Na[Mn(CO)_5]$, $K_2[Fe(CO)_4]$, $K[Co(CO)_4]$, etc., the carbonyl anions of which have been discussed individually above.

The corresponding compounds of the heavy metals such as $Zn[Co(CO)_4]_2$, $Ga[Co(CO)_4]_3$, $Hg[Mn(CO)_5]_2$, etc., are believed, however, to be covalent and to contain non-transition to transition metal bonds.[138]

Reactions of the tetracarbonylferrate ion with compounds of arsenic, antimony, bismuth, tin, lead, thallium, etc., have been reported to give a remarkable series of compounds exemplified by $PbFe_3(CO)_{12}$, $SbFe_2(CO)_8$, $Sn_2Fe_5(CO)_{20}$, etc. and some of the species formed, such as $As_2Fe_3(CO)_{12}$ and $SbFe_2(CO)_8$, are reported to be paramagnetic. Structures for some of these compounds have been proposed.[139]

The only mixed neutral carbonyl consisting simply of two different transition metals and carbon monoxide which has been synthesised[140] to date is cobalt manganese enneacarbonyl, $CoMn(CO)_9$. It is likely that this compound consists of the $Co(CO)_4$ moiety and the $Mn(CO)_5$ moiety joined solely by a metal–metal bond. It was prepared by the interaction of the compounds $Na[Co(CO)_4]$ and $Mn(CO)_5Br$. This reaction, by condensation of alkali halide, to form a metal–metal bond between two different transition metals, was first used[141] in the preparation of the compound $(\pi\text{-}C_5H_5).W(CO)_6.Mo(\pi\text{-}C_5H_5)$, and has subsequently[140, 142] been used to prepare the following complexes: $\pi\text{-}C_5H_5.Fe(CO)_5.Mo(\pi\text{-}C_5H_5)$, $(\pi\text{-}C_5H_5).Fe(CO)_2.Mn(CO)_5$, $Co.Mn(CO)_9$, and $\pi\text{-}C_5H_5.Fe(CO)_2.Co(CO)_3$.

Dicyclopentadienylnickel reacts with iron pentacarbonyl to give a complex $(\pi\text{-}C_5H_5).Fe(CO)_3.Ni(\pi\text{-}C_5H_5)$, which contains an iron–nickel bond and two bridging carbonyl groups.[143]

The complex ion $[Fe.Co_3(CO)_{12}]^{2-}$ obtained by interaction of iron

[136] Hieber, Kroder, and Zahn, *Z. Naturforsch.*, 1960, **15b**, 325; Hieber and Braun, *ibid.*, 1959, **14b**, 132.
[137] Behrens and Lohöfer, *Chem. Ber.*, 1961, **94**, 1391.
[138] Stammreich, Kawai, Sala, and Krumholz, *J. Chem. Phys.*, 1961, **35**, 2175.
[139] Hieber, Gruber, and Lux, *Z. anorg. Chem.*, 1959, **300**, 275.
[140] Joshi and Pauson, *Z. Naturforsch.*, 1962, **17b**, 565.
[141] Abel, Singh, and Wilkinson, *J.*, 1960, 1321.
[142] Treichel and Stone, *Chem. and Ind.*, 1961, 747.
[143] Tilney-Bassett, *Proc. Chem. Soc.*, 1960, 419.

and cobalt carbonyls in acetone is believed to have a structure similar to that already proposed for $Co_4(CO)_{12}$, in which one cobalt atom is replaced by iron.[144]

In view of the stability of the mixed metal carbonyl derivatives already reported, many other neutral carbonyls such as $(CO)_5Re.Mn(CO)_5$,* and anionic species such as $[(CO)_5Mo.W(CO)_5]^{2-}$ should be sufficiently stable to be isolated under the right experimental conditions.

* *Added in Proof.*—This carbonyl has now been reported (Nesmeyanov, Anisimov, Kolobova, and Kolomniker, *Izvest, Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1963, 194).

[144] Chini, Colli, and Peraldo, *Gazzetta*, 1960, **90**, 1005.